Designing Kitaev Spin Liquids in Metal-Organic Frameworks

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Designing Kitaev spin liquids in metal-organic frameworks

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Kitaev's honeycomb lattice spin model is a remarkable exactly solvable model, which has a particular type of spin liquid (Kitaev spin liquid) as the ground state. Although its possible realization in iridates and α-RuCl$_3$ has been vigorously discussed recently, these materials have substantial non-Kitaev direct exchange interactions and do not have a spin liquid ground state. We propose metal-organic frameworks (MOFs) with Ru^{3+} (or Os^{3+}) forming the honeycomb lattice as promising candidates for a more ideal realization of Kitaev-type spin models where the direct exchange interaction is strongly suppressed. The great flexibility of MOFs allows generalization to other three-dimensional lattices, for potential realization of a variety of spin liquids such as a Weyl spin liquid.

PhySH: Frustrated magnetism, Spin liquid, Quantum spin liquid, Organic compounds

Introduction. — Quantum spin liquids, purported exotic states of quantum magnets where long-range magnetic orders are destroyed by quantum fluctuations, have been a central subject in quantum magnetism [1]. As an important theoretical breakthrough, Kitaev constructed a spin-1/2 model on the honeycomb lattice [2] with Ising interactions between spin components depending on bond orientations. Its exact solution demonstrates many intriguing properties such as fractionalized anyonic excitations. This model was later generalized to other lattices, including three-dimensional ones, still retaining the exact solvability [3]. In this paper, we call this type of model including various generalizations as Kitaev model, and its ground states as Kitaev spin liquids.

Jackeli and Khaliullin [4] discovered that the "Kitaev interaction", namely bond-dependent Ising couplings, can be realized in a (111) honeycomb layer of iridates, i.e. the A_2IrO$_3$ (A = Na, Li) structure, by the superexchange interaction through the oxygen ions due to the strong spin-orbit coupling of Ir^{4+} in the Mott insulator limit (see also Ref. [5] for the itinerant limit).

However, unfortunately, it turned out that iridates and related inorganic compounds, such as α-RuCl$_3$ [6], exhibit a conventional magnetic order at low enough temperatures and do not have a true spin liquid ground state. This is due to the non-Kitaev interactions, such as antiferromagnetic Heisenberg interaction, mainly coming from the direct exchange interaction between the metal ions [7]. While their finite-temperature properties still reflect the proximity to the Kitaev model [8] and thus are of great interest, the current situation calls for a more ideal realization of the Kitaev model in real materials, so that they exhibit spin liquid ground states.

In this Letter, we propose such a possible realization of the Kitaev model in metal-organic frameworks (MOFs), crystalline materials consisting of metal ions and bridging organic ligands. Although MOF is a central subject in modern complex chemistry, MOFs have not attracted much attention in the context of magnetism. This is perhaps because they do not show any magnetic ordering at room temperature as direct exchange interactions between magnetic metal ions are suppressed and the remaining indirect superexchange interactions via nonmagnetic organic ligands are weak. We take the advantage of this suppression of direct exchange interactions to realize the Jackeli-Khaliullin mechanism, i.e. superexchange realization of the Kitaev interaction. Furthermore, based on tight-binding models and the fragment molecular orbital (fMO) method [9] in combination with the density functional theory (DFT) calculations, we demonstrate that the Jackeli-Khaliullin mechanism gives rise to the dominant Kitaev interactions with oxalate-based (or tetraaminopyrazine-based) ligands. This opens up the possibility of *designing* the appropriate MOFs to realize Kitaev spin liquids.

Structures of the Proposed Metal-Organic Frameworks. — In order to realize a Kitaev spin liquid in MOFs using the Jackeli-Khaliullin mechanism [4], we first propose an MOF structure with Ru^{3+} (or Re^{2+}, Os^{3+}, Rh^{4+}, Ir^{4+}) ions in the octahedral coordination. Because of the composite effects of the octahedral ligand field and the strong spin-orbit coupling, these $4d^5$ or $5d^5$ ions show a low-spin ground state with an effective angular momentum $J_{\mathrm{eff}} = 1/2$. Hinted by the (111) honeycomb layers of iridates, we propose a geometric structure shown in Fig. 1(a), where the RuO$_6$ octahedra form a two-dimensional (2D) honeycomb lattice and the organic ligand (in this case oxalate, (C$_2$O$_4$)$^{2-}$, or ox^{2-}) connects the two edges of the octahedra. Indeed, many honeycomb MOFs with this structure have already been found by chemists [10–21]. More interestingly, this honeycomb structure of metal-oxalate frameworks is also found in nature in the form of minerals, stepanovite and zhemchuzhnikovite [22]. Thus, we can expect that this honeycomb geometry is chemically stable. Moreover, experiments [23] for the molecule $[\{\mathrm{Ru(acac)_2}\}_2(\mu\text{-ox})]^-$ (acac$^-$ = acetylacetonate) observed an anisotropic spin interaction via oxalate due to the spin-orbit coupling of Ru^{3+}

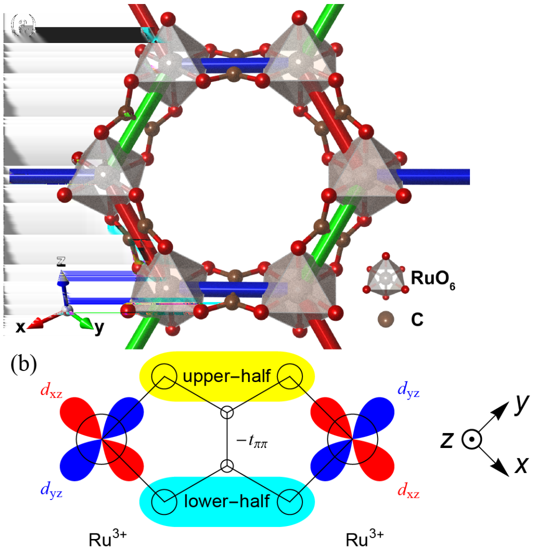

FIG. 1. (Color online) (a) Geometric structure of honeycomb Ru-oxalate frameworks. White octahedra are RuO_6 octahedra and carbon atoms are shown in brown. The color of the bond between the Ru atoms means which plane the bridging oxalate belongs to (red: yz-plane, green: zx-plane, blue: xy-plane). (b) Two superexchange pathways between two neighboring Ru^{3+} through an oxalate ion belonging to the xy-plane (one of the blue bonds in (a)). $t_{\pi\pi}$ is a hopping parameter between the two distinct pathways.

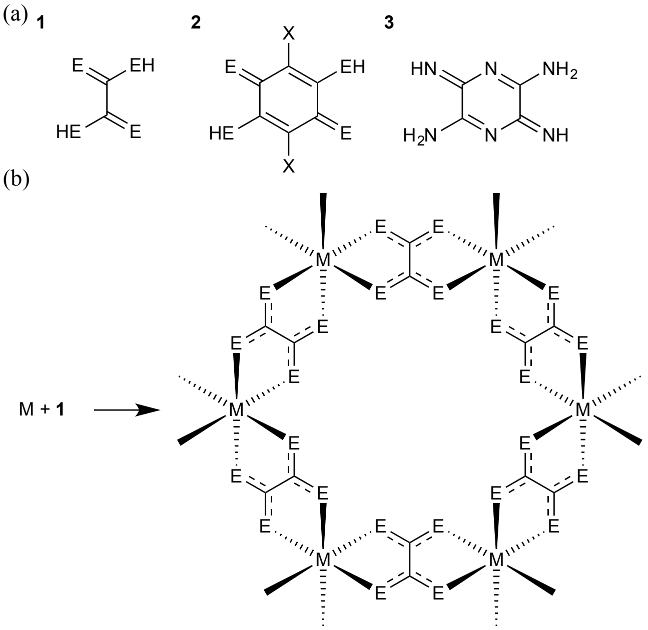

FIG. 2. Chemical formulae for the proposed metal-organic frameworks. (a) Possible organic molecules to realize a honeycomb structure with octahedral coordination. **1**: Oxalate-based molecules (E = O, S, NH). **2**: Quinoid-based molecules (E = O, S, NH; X = H, Cl, Br, I, etc.). **3**: Tetraaminopyrazine-based molecule. (b) Honeycomb structure of metal-oxalate frameworks (M = Ru, Os).

with electron spin resonance. Similar anisotropy has also been observed in many other Ru and Os complexes [24]. It is, therefore, natural to consider Ru and oxalate to realize the Kitaev interaction, as the first candidate.

The ligand can be replaced with other organic molecules to achieve a wide variety of MOFs. Some possibilities, including a newly proposed one, are listed in Fig. 2(a) for MOFs with Ru^{3+} (or Os^{3+}) in the octahedral coordination. In Fig. 2(a), **1** is oxalic acid (E = O) and becomes oxalate in the proposed MOF (see Fig. 2(b)). In the case of E = S (resp. NH), we call it tetrathiooxalate (resp. tetraaminooxalate). Similarly, **2** becomes dhbq^{2-} (E = O, X = H and dhbq = 2,5-dihydroxy-1,4-benzoquinone) or X_2An^{2-} (E = O, X = Cl, Br, etc. and An = anilate), and **3** is tetraaminopyrazine $C_4N_6H_6$ and becomes $(C_4N_6H_4)^{2-}$, which we have newly proposed. There already exists a metal-oxalate framework including Ru^{3+}, such as $LaRu(ox)_3{\cdot}10H_2O$ in Ref. [20], and the molecule $[Ru(ox)_3]^{3-}$ is known to be a good spin-1/2 qubit [25], so it is very natural to use this $Ru(ox)_3$ unit as a building block for highly entangled quantum states. In any M_2L_3 (M = Ru, Os, and L = ox, dhbq, etc.) structures, the metal ion M should be in the 3+ state and the organic ligand L should be in the 2− state. Additional structures may be necessary to maintain the rigid honeycomb structure for M_2L_3 layers, but it will not affect the effective spin model as long as Ru or Os is in the 3+ state and the interlayer interaction is negligible. In fact, in the Fe^{3+}-based MOF with layered structure discovered in Ref. [21], the interlayer distance of metal ions is as large as 8.7449 Å, and the interlayer interaction is found to be negligible or ferromagnetic.

Superexchange Interaction. — The main obstacle to realize Kitaev spin liquids in inorganic materials was the direct exchange interaction between the metal ions, which yields significant non-Kitaev interactions [7]. In MOFs, the electron density of the bridging organic ligand screens the wavefunction tails of the metal ions, which would substantially reduce the direct overlap between orbitals of the neighboring metals. Thanks to this, the direct exchange interaction is strongly suppressed in most MOFs [21]. This is the most important advantage of using organic ligands for the realization of Kitaev spin liquids compared to other inorganic candidates, such as iridates and α-$RuCl_3$. However, non-Kitaev interactions can also arise from the superexchange interaction. In order to evaluate the magnitude of those terms, we derive the effective spin Hamiltonian in the following steps. First we obtain the effective tight-binding model for the superexchange between two Ru ions, and then we map this model into the effective spin model. As a concrete example, we take one specific bond belonging to the xy-plane shown in Fig. 1(b) in the following discussions.

As we will see below, Jackeli-Khaliullin mechanism works perfectly to give rise to the pure Kitaev interaction, if there are two separate superexchange pathways connecting d_{xz} and d_{yz} only. The advantage of using oxalate as the ligand is the existence of the localized modes along upper- and lower- edges of the molecule, which are analogous to the localized edge modes along the zigzag edges of graphene [26]. They can function as the desired two superexchange pathways. In fact, the separation of the two paths is not perfect and we have to consider the effect of their mixing quantitatively. Nevertheless, as we will demonstrate, the mixing is small and the two superexchange pathways are approximately protected. This leads to a dominant Kitaev interaction.

In the chemical terminology, we may consider two "fragment molecular orbitals" (fMO) [9] corresponding to these localized edge modes. For simplicity, here we focus on HOMOs (highest occupied molecular orbitals) and LUMOs (lowest unoccupied molecular orbitals) coming from π-orbitals (π-HOMO and π^*-LUMO for short, respectively), which are the most important as superexchange pathways between Ru^{3+} ions. With the annihilation operators u and l, respectively, for π-HOMOs along upper- and lower-edges in Fig. 1(b), the model Hamiltonian may be written as

$$\begin{aligned} H_{d\pi} = &-t_{d\pi}(u^\dagger d^L_{yz} + l^\dagger d^L_{xz} + u^\dagger d^R_{xz} + l^\dagger d^R_{yz} + h.c.) \\ &+ V_\pi(u^\dagger u + l^\dagger l) - t_{\pi\pi}(u^\dagger l + l^\dagger u), \end{aligned} \tag{1}$$

where $t_{d\pi}$ is the hopping matrix element between the Ru t_{2g}-orbitals and the π-HOMOs, V_π is the energy level of π-HOMOs, $t_{\pi\pi}$ is the tunneling matrix element between the two fMOs, d^L_i (resp. d^R_i) is the annihilation operator of an electron on the Ru d_i-orbital on the left (resp. right) side in Fig. 1(b). Similar terms exist for the π^*-LUMO with the energy level V_{π^*} or the hopping and tunneling matrix elements $t_{d\pi^*}$ and $t_{\pi^*\pi^*}$, respectively. If the separation of the two paths were perfect, then $t_{\pi\pi} = 0$, but in reality it is non-vanishing. Thus the energy levels of HOMOs are split into $V_\pi \pm t_{\pi\pi}$. Nevertheless, reflecting the approximate protection of the two pathways, $t_{\pi\pi}$ is relatively small. This can be confirmed by the DFT calculations, as we will discuss later.

Integrating over the π-HOMO states u and l, we obtain the effective hopping terms between the two Ru^{3+} ions as

$$\begin{aligned} H_{dd} = &- t_1(d^{L\dagger}_{yz} d^R_{yz} + d^{L\dagger}_{xz} d^R_{xz}) - t_2(d^{L\dagger}_{yz} d^R_{xz} + d^{L\dagger}_{xz} d^R_{yz}) \\ &- t_3 d^{L\dagger}_{xy} d^R_{xy} + h.c., \end{aligned} \tag{2}$$

where $t_1 = t^2_{d\pi} t_{\pi\pi}/(V^2_\pi - t^2_{\pi\pi})$, $t_2 = t^2_{d\pi} V_\pi/(V^2_\pi - t^2_{\pi\pi})$, and $t_3 = 0$. As expected, t_1/t_2 is small when $t_{\pi\pi}$ is small. We should also include the superexchange contributions through π^*-LUMO and σ-orbitals in deriving the effective hopping terms.

Once we obtain the effective hopping (2), by projecting onto $J_{\text{eff}} = 1/2$ states of Ru^{3+}, we can derive the effective spin model [27]

$$H = \sum_{\langle ij\rangle \in \alpha\beta(\gamma)} [J \boldsymbol{S}_i \cdot \boldsymbol{S}_j + K S^\gamma_i S^\gamma_j + \Gamma(S^\alpha_i S^\beta_j + S^\beta_i S^\alpha_j)], \tag{3}$$

where J is the Heisenberg coupling, K is the Kitaev coupling, and Γ is the symmetric off-diagonal exchange. The explicit form of these parameters is included in Supplemental Material. $\alpha, \beta, \gamma \in \{x, y, z\}$ and $\langle ij\rangle \in \alpha\beta(\gamma)$ mean that the bond plane of the nearest-neighbor bond $\langle ij\rangle$ is the $\alpha\beta$-plane perpendicular to the γ-axis. This model is an extended version of the Kitaev-Heisenberg model [28], known as the JKΓ model [27, 29]. In the limit $J/|K| \to 0, \Gamma/|K| \to 0$, the model is nothing but the honeycomb Kitaev model [2], which has a gapless spin liquid ground state. Here we ignore Dzyaloshinskii-Moriya interactions, assuming the parity symmetry around the bond center.

In this way, we can estimate the parameters J, K, and Γ starting from the fMO-based model (1) of the ligand. As we have emphasized, if the superexchange paths along the upper- and lower- halves were completely separate, $t_{\pi\pi} = t_{\pi^*\pi^*} = 0$ which would give $t_1 = t_3 = 0$. With the effective hopping (2) with only t_2 non-vanishing, Jackeli-Khaliullin mechanism works perfectly and we would obtain the ideal Kitaev model with $J = \Gamma = 0$. This condition could easily be met by using two formates as bridging ions, each of which acts as a separate superexchange pathway, although the honeycomb structure may be unstable in metal-formate frameworks.

Estimation of Spin Interactions. — In order to estimate the parameters in the effective spin model (3) in real MOFs proposed in Fig. 2, we have performed DFT calculations for the oxalate ligand using OPENMX [30] software package. It should be noted that a calculation on a ligand molecule only gives the energy differences such as $V_{\pi^*} - V_\pi$. The individual energy levels such as V_{π^*} and V_π measured from the Fermi level, i.e. the Ru $J_{\text{eff}} = 1/2$ orbital, cannot be directly obtained.

In this work, as a crude but quick estimate to see the potential of our proposal, we will proceed as follows. In the case of oxalate, for example, $V_{\pi^*} - V_\pi = 6.47$ eV from DFT. Experiments [23] suggest that the metal to ligand charge transfer (MLCT) energy $E_{\text{LUMO}} = V_{\pi^*} - t_{\pi^*\pi^*} \sim 2.6$ eV, which corresponds to the optical absorption at the wavelength of 485 nm. This, together with $t_{\pi\pi} = 0.153$ eV and $t_{\pi^*\pi^*} = 1.631$ eV from the DFT calculations, implies $V_{\pi^*} \sim 4.2$ eV and $V_\pi \sim -2.3$ eV. Using these parameters, and $t_{d\pi^*}/t_{d\pi} \sim 0.6159$ for oxalate, we find the ratio between the effective hoppings in Eq. (2) as

$$\frac{t_1}{t_2} = \frac{\frac{t^2_{d\pi} t_{\pi\pi}}{V^2_\pi - t^2_{\pi\pi}} - \frac{t^2_{d\pi^*} t_{\pi^*\pi^*}}{V^2_{\pi^*} - t^2_{\pi^*\pi^*}}}{\frac{t^2_{d\pi} V_\pi}{V^2_\pi - t^2_{\pi\pi}} - \frac{t^2_{d\pi^*} V_{\pi^*}}{V^2_{\pi^*} - t^2_{\pi^*\pi^*}}} \sim 0.023. \tag{4}$$

Taking the superexchange via σ-orbitals into account in a similar manner, we find $t_3/t_2 \sim -0.196$. From these values, we estimate $J/|K| \sim 0.004$ and $|\Gamma|/|K| \sim 0.15$, namely the Kitaev interaction is strongly dominant. The details of the derivation is given in Supplemental Material.

In general, we find that the resulting low-energy effective model is dominated by the Kitaev interaction ($J/|K| \sim |\Gamma|/|K| \lesssim 1/10$), if the conditions $|t_{\pi\pi}|/|V_\pi| \lesssim 1/10$ and $|V_\pi|/|V_{\pi^*}| \lesssim |t_{d\pi}\sqrt{t_{\pi\pi}}|/|t_{d\pi^*}\sqrt{t_{\pi^*\pi^*}}|$ are both met. We note that the smallness of $|V_\pi|/|V_{\pi^*}|$ implies that the superexchange is hole-mediated [31].

Although there is no particular reason to have degeneracy in aromatic ligands, such as dhbq^{2-} and X_2An^{2-} (**2** in Fig. 2(a)), it is possible to have similar degeneracy of π-HOMOs in the tetraaminopyrazine-based ligand $(C_4N_6H_4)^{2-}$ (**3** in Fig. 2(a)). In contrast to oxalate, the degenerate two π-HOMOs are just below the Fermi energy even in the vacuum, so tetraaminopyrazine-based structures should also be good candidates for Kitaev-dominant MOFs. In addition, this $(C_4N_6H_4)^{2-}$ would stabilize the planar structure more easily than oxalate due to the π-conjugated nature.

While the present estimate is crude and we have ignored many possible corrections, these results suggest that our proposal of realizing Kitaev spin liquids in MOFs is quite promising. We emphasize that, MOFs have the flexibility in the choice of ligand molecules, so that many possibilities can be tried for the realization of Kitaev spin liquids.

Designing a Variety of Kitaev Spin Liquids. — Here we emphasize another advantage of MOFs: we can construct various complex geometric structures, not limited to the honeycomb lattice, by self-organization. In particular, three-dimensional (3D) generalizations of the Kitaev model are of great interest [32]. A realization in iridates has been reported but again with a magnetic ordering at low temperatures [33]. One of the 3D structures known as the hyperhoneycomb lattice or (10,3)-b is, on the other hand, naturally realizable in MOFs, such as $[(C_2H_5)_3NH]_2Cu_2(C_2O_4)_3$ shown in Fig. S1 in Supplemental Material, and can in principle be constructed just by putting building blocks altogether and stirring [34]. The cation-templating is known to be important to construct a 3D structure [34], so we would possibly need to replace Cu^{2+} with Re^{2+} rather than with Ru^{3+}. The analysis in the previous section can also be applied to MOFs with 3D tricoordinated lattices, to derive the same JKΓ model as the effective low-energy spin model on the corresponding lattice.

By applying a magnetic field to break the time-reversal symmetry, the system with a 3D hyperhoneycomb lattice is expected to show a gapless Weyl spin liquid ground state [35]. More interestingly, there are other 3D tricoordinated lattices with exotic Majorana states, which have not been found in iridates but are possible in 3D MOFs. Among these, the hyperoctagon lattice or (10,3)-a structure [36–43] has Majorana Fermi surfaces, which would be destabilized by an additional time-reversal interaction leaving an odd number of nodal lines [44, 45].

Finally, we would like to discuss the possibility to realize gapped spin liquid ground states, i.e. topological phases with ground state degeneracy. Kitaev [2] pointed out that a non-Abelian gapped topological phase would emerge from the honeycomb Kitaev model by applying a magnetic field along the [111] direction in Fig. 1(a), and an Abelian gapped Z_2 topological phase, described by the toric code [46], can be induced by introducing the bond anisotropy, i.e. breaking the three-fold symmetry of the system. The former situation is simply expected when we apply an external magnetic field to the proposed honeycomb MOFs in the same way as iridates. Concerning the latter possibility of the gapped Abelian Z_2 topological phase, realization in iridates would require an application of a uniaxial strain, which turns out to be experimentally difficult. In contrast, in MOFs, the bond anisotropy may be introduced chemically using heterogeneous organic ligands, leading to the Z_2 topological phase, as we present details in Supplemental Material. An example of possible MOF structures with heterogeneous ligands is shown in Fig. S6. Similar distorted honeycomb MOFs with heterogeneous ligands were already reported [47], so we expect that the materials proposed here could be synthesized.

Conclusion. — We discussed the possibility to realize Kitaev spin liquids in MOFs and found three advantages over inorganic materials: the suppression of undesired direct exchange interactions, the flexibility to control the parameters using a variety of possible ligands, and the natural realization of complex structures. All of these features of MOFs will pave a way towards an experimental realization of the exotic Kitaev spin liquids as the ground states, one of the holy grails in contemporary condensed matter physics.

Due to the large unit cell of MOFs, similarly to new Kitaev-dominant iridates with a longer Ir — O — O — Ir superexchange [48], the energy scale of the superexchange interaction will be 10–100 K. The finite-temperature phase transition into the Kitaev spin liquid phase in the 3D case is expected at 1/100 of this energy scale [49], namely at 0.1–1 K. Although this will make the experimental studies of the Kitaev spin liquid phase below this temperature somewhat challenging, it is still possible as it is reachable with a dilution refrigerator.

Our proposal opens up many questions. We have not discussed the geometric stability of the proposed MOFs, but there is no obvious obstacle for realization of metal-oxalate frameworks with Ru^{3+} considering many reports of synthesizing metal-oxalate frameworks with various metals [11, 13, 19, 20, 34, 37–40, 43]. In fact, honeycomb MOFs with $R3c$ and $P6/mmm$ space groups, which respect a full symmetry of the honeycomb lattice, was realized with the high-spin Fe^{3+} ions [11]. We can thus naturally expect that replacement by the low-spin Ru^{3+} would not lead to any lattice distortions from the idealized case [50] because of the proximity of the ionic radii, in contrast to honeycomb iridates with small monoclinic distortions [27]. It is still subtle whether a possible trigonal distortion [51], which does not break any space group symmetry, supports the formation of our proposed structure to stabilize the spin liquid states [52, 53]. Assuming the effect of the trigonal distortion of the $\mathrm{RuO_6}$ octahedra in MOFs is the same as that in iridates, a recent study [27] discovered that the Kitaev term would dominate when $\angle$ (O — Ru — O) $\sim 80^\circ$, which quite agrees with the observed values in MOFs [54]. In any case, we will need a more rigorous first-principles calculation with geometric optimization.

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